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Synthesis and characterization of poly[oxy-(2,5-dibenzoyl-1,4-phenyleneoxy)-1,4-phenylene]

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Poly[oxy-(2,5-dibenzoyl-1,4-phenyleneoxy)-1,4-phenylenel] (**3**) was prepared by the aromatic nucleophilic substitution reaction of 2,5-difluoro-4-benzoylbenzophenone (**2**) with hydroquinone (**1**) in the presence of potassium carbonate in diphenylsulfone. The polycondensation was conducted at 150–320°C for 4 h and produced polymer **3** at excellent yield levels. Polymer **3** was characterized by elemental analysis, i.r. spectroscopy, differential scanning calorimetry (d.s.c.) and wide angle X-ray measurement (WAXD). Polymer **3** showed two endothermic peaks on d.s.c. scans, which would be attributable to recrystallization effects; the lower-temperature endotherm represented only a portion of the melting endotherm of original crystals and the upper-temperature endotherm was the melting of crystals reorganized during a heating scan. © 1997 Elsevier Science Ltd.

(Keywords: double-melting endotherms; pendant benzoyl groups; poly(arylene ether)s)

INTRODUCTION

High temperature polymers containing phenylene groups in the main chain are currently of interest as thermoplastic matrix materials in composites for engineering purposes[1–3]. Poly(ether ether ketone) (PEEK) is one of them. Its semicrystalline structure with an unusual combination of properties, such as high chemical resistance, excellent thermal stability and good mechanical properties, makes it a very interesting compound. For the synthesis of poly (arylene ether ketone) analogues, higher boiling solvents, such as diphenylsulfone, have been used to avoid premature crystallization of oligomers and give high molecular weights under rather severe conditions (> 320°C)[4].

We are interested in the synthesis and properties of poly(arylene ether)s with keto-aryl pendant groups which are constitutional isomers of poly(arylene ether ketone) analogues. In a previous paper, we have reported the synthesis of poly[oxy-(2,5-dibenzoyl-1,4-phenyleneoxy)-1,4-phenylene] **3** in DMAC at 170°C[5]. Interestingly, the thermal properties, such as T_g and T_m, of polymer **3** were comparable to those of PEEK. However, the molecular weight was relatively low because of the limited solubility of polymer **3** in the reaction medium.

In this paper, we describe the successful synthesis of polymer **3** with a high molecular weight by a high-temperature solution polycondensation using diphenylsulfone as a solvent. Furthermore, the melting and crystallization behaviour of polymer **3** are discussed as compared with those of poly(arylene ether ketone) analogues.

EXPERIMENTAL

Materials

Hydroquinone was purified by multiple sublimations. Diphenylsuifone was recrystallized from diethylether. The other reagents and solvents were obtained commercially and used as received.

Monomer synthesis

2,5-Difluoro-4-benzoylbenzophenone (**2**) was prepared by a reaction of 2,5-difluoroterephthaloyl chloride with benzene in a manner previously described[5].

Polymer synthesis

Into a 25 ml, two-necked, round-bottom flask equipped with a stirrer, an argon inlet and a condenser was placed **2** (0.322 g, 1.00 mmol), potassium carbonate (0.139 g, 1.01 mmol), hydroquinone (0.110 g, 1.00 mmol) and diphenylsulfone (1.5 g). The mixture was initially heated at 150°C for 1 h, the reaction temperature was raised 50°C every hour, and was finally heated at 320°C for 30 min. The hot mixture was poured into a pan, cooled, ground to a fine powder, extracted with boiling acetone and boiling water, and dried overnight under vacuum at 100°C. Yield = 90%. Infrared (KBr): 1194, 1244, 1480, 1582 and 1669 cm^{-1}. Analysis: calculated for $(C_{26}H_{16}O_4)_n$: C, 79.58%; H, 4.11%. Found: C, 79.40%; H, 4.17%.

*Chloromethylation of polymer (**4**)*

Tin (IV) chloride was added to a suspension of polymer (200 mg, 0.273 mmol) in 1,4-bis(chloromethoxy)butane (2.0 ml) and was stirred for 12 h at room temperature and carefully quenched with water. The organic layer was

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*To whom correspondence should be addressed washed with water, dried with $MgSO_4$ and the solvent was evaporated. The polymer was obtained in quantitative yield. Purification of the polymer was carried out by washing with water, followed by Soxlet extractions with the mixture of methanol and chloroform (v/v = 5/1). ^1H n.m.r. ($CDCl_3$) δ: 4.20 (s, 2H), 6.75–6.95 (m, 3H), 7.36–7.76 ppm (m, 10H). Analysis: calculated for $(C_{27}H_{17}O_4Cl)_n$: C, 73.56%; H, 3.89%. Found: C, 73.90%; H, 4.02%.

Sample preparation and thermal analysis

In order to cancel the thermal history of polymerization, all samples were melted at 400°C and were cooled at $10°C\ min^{-1}$ before various following treatment. The amorphous sample was prepared by quenching into MeOH/dry ice (– 78°C) from the melt. Annealed samples were obtained by treating at various temperature (220–300°C) for 1 h. Another set of samples was heated at various melt–annealing temperatures (350–380°C), held for 30 min, and then cooled at $10°C\ min^{-1}$. Heating rate experiments were carried out using samples which were annealed at 240°C for 1 h.

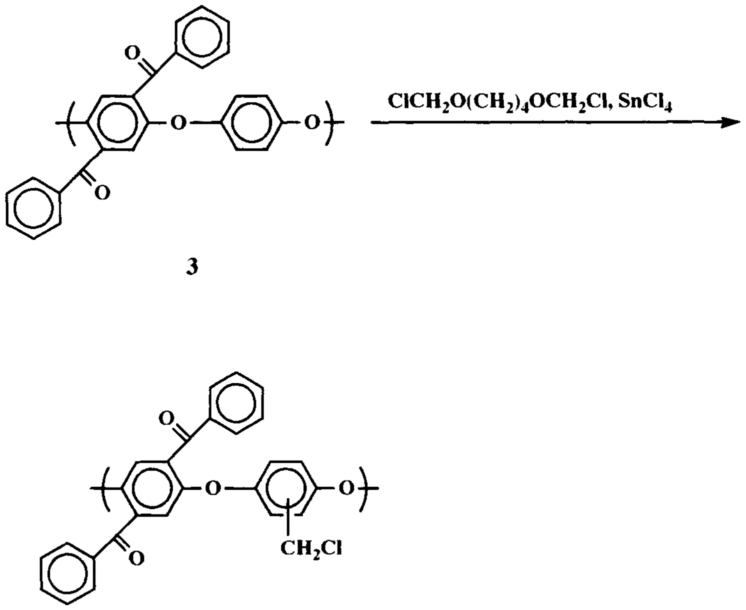
Measurements

Infrared spectra were obtained on a Horiba FT-210 infrared spectrometer and all nuclear magnetic resonance spectra were obtained using a JEOL EX 270 spectrometer. Thermal analyses were performed on a Seiko SSC/5200 (TG/DTA 220) thermal analyser at a heating rate of $10°C\ min^{-1}$ for thermogravimetric analysis (t.g.a.). The glass transition, melting and crystallization temperatures were measured under various heating rates and $-10°C\ min^{-1}$ cooling rate on a Seiko SSC/5200 (d.s.c. 200). To minimize complications arising from the low thermal conductivity of polymers, the sample size for the polymer was restricted to 0.5–1.0 mg. All crystallizations and heating and cooling scans were done under a nitrogen purge. Molecular weights were determined by size exclusion chromatography (s.e.c.) in DMF with polystyrene calibration using a TOSOH HLC-8120 equipped with a TOSOH TSK gel GMH_{HR}-M column at 40°C. The measurements of density were carried out using a hydrometer in a mixture of methanol and carbon tetrachloride. X-ray diffraction experiments were performed on a RAD-rA diffractometer (Rigaku Denki Co. Ltd.) using powder or film samples. Nickel-filtered CuKα radiation was employed. The wide angle X-ray diffraction (WAXD) traces were recorded by a scintillation counter system with a 1.0 mm diameter pin-hole collimator. The small angle X-ray diffraction (SAXS) experiments were carried out using a first slit (2.0 mm) and a second slit (1.5 mm), and the camera distance was 200 mm.

RESULTS AND DISCUSSION

Polymer synthesis and properties

As described in the Introduction, high temperature solution condensations using diphenylsulfone as a solvent is a suitable method to avoid premature crystallization of oligomers during a polymerization, resulting in high molecular weight of polymers. The polycondensation of 2,5-difluoro-4-benzoylbenzophenone (**2**) with hydroquinone (**1**) was carried out in diphenylsulfone [equation (1)].



3

4

(1)

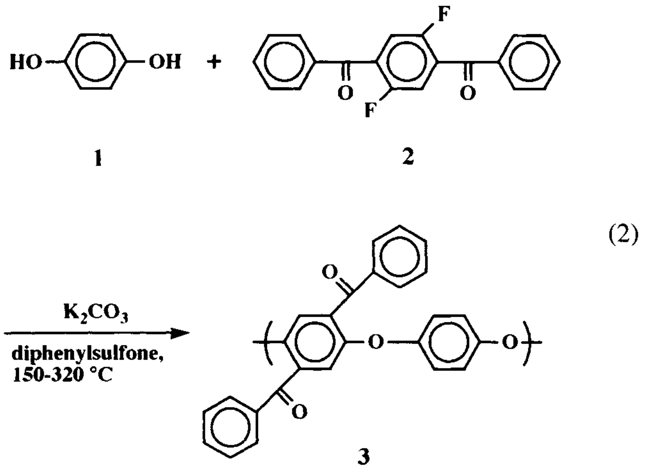
The reaction temperature was initially started at 150°C to avoid sublimation of monomers, raised slowly to 320°C at a heating rate of $50°C\ h^{-1}$, and then kept at this temperature for 30 min. The polycondensation proceeded without precipitation of polymer, giving the desired polymer in excellent yield.

Polymer **3** was confirmed to be the corresponding poly(arylene ether) by i.r. spectroscopy and elemental analysis. The i.r. spectrum exhibited characteristic absorptions at 1666 and $1180\ cm^{-1}$ due to C=O and C–O–C stretching, respectively. Elemental analysis also supported the formation of the expected polymer.

Polymer **3** was a faint grey solid and soluble only in pentafluorophenol.

Chloromethylation of polymer **3**

A limited solubility of polymer **3** prevented the more detailed characterization. Electrophilic reactions involving chloromethylation and sulphonation of poly(arylene ether ketone)s are versatile routes to polymer modification[6]. Thus, polymer **3** was chloromethylated to increase its solubility in organic solvents. The chloromethylation of polymer **3** was carried out using bis(chloromethoxy)butane in the presence of a catalytic amount of tin chloride. This reaction gave the desired soluble polymer **4** [equation (2)] in organic solvents including DMF, chloroform and THF.



(2)

The n.m.r. spectrum of polymer **4** showed signals at 4.20, 6.75–6.95 and 7.36–7.76 ppm due to chloromethyl groups, hydroquinone and benzoyl units, respectively (*Figure 1*). From the integration ratio between chloromethyl and aromatic protons, it was found that the chloromethylation occurred quantitatively on aromatic rings of the hydroquinone moiety (chloromethyl monomeric unit = 1:1). This structure was also supported by elemental analysis.

The molecular weight of polymer **4** was determined by size exclusion chromatography (s.e.c.). An unimodal molecular weight distribution was observed. The chromatograph of polymer **4** indicated that the relative MW values was 60 000 and the distribution of molecular weight was 4.1, relative to polystyrene standards.

Thermal properties

The thermal properties of polymer **3** were examined by thermogravimetry (t.g.a.) and differential scanning calorimetry (d.s.c.) on a powder sample. These data are listed in *Table 1*. The decomposition temperature (the 10% weight loss temperature) of polymer **3** was 470°C in a nitrogen atmosphere.

The d.s.c. for the as-made sample of polymer **3** exhibited only a slight change of baseline at 140°C and a endothermic peak at 338°C due to the glass transition (T_g) and melting temperature (T_m), respectively. These T_g and T_m values are comparable to those of PEEK.

Melting behaviour of polymer **3**

It has been known that several polymers including PEEK exhibited two distinct melting endotherms during differential thermal analysis. A variety of explanations for this behaviour have been proposed[7–10]. Two of these are: (i) the peaks are associated with two distinct crystals or morphologies; and (ii) the peaks are related to a melting and recrystallization phenomenon of one initial crystal morphology which is characteristic of the prior crystallization history. Therefore, the melting behaviour of polymer **3** was investigated. *Figure 2* shows d.s.c. heating scans for a series of samples that had been annealed at different temperatures (220–300°C) for 1 h. These results are summarized in *Table 2*. Two endothermic melting peaks were observed for all samples. Annealing treatment shifted the lower peak upwards to about 10°C above the annealing temperature. On the other hand, the main upper peak remained unchanged as a result of the annealing treatment. This annealing behaviour is very similar to that of PEEK.

Polymer **3** samples, which had been isothermally crystallized at 240°C for 1 h, were scanned at different heating rates. The peak temperatures and heats of fusion of the

Table 1 Thermal properties for polymer 3

T_g (°C)	T_m (°C)	Decomposition temperature (°C)[a] Air	N_2
140	338	470	470

[a] Temperature at which a 10% weight loss was recorded by t.g.a. at a heating rate of 10°C min^{-1}

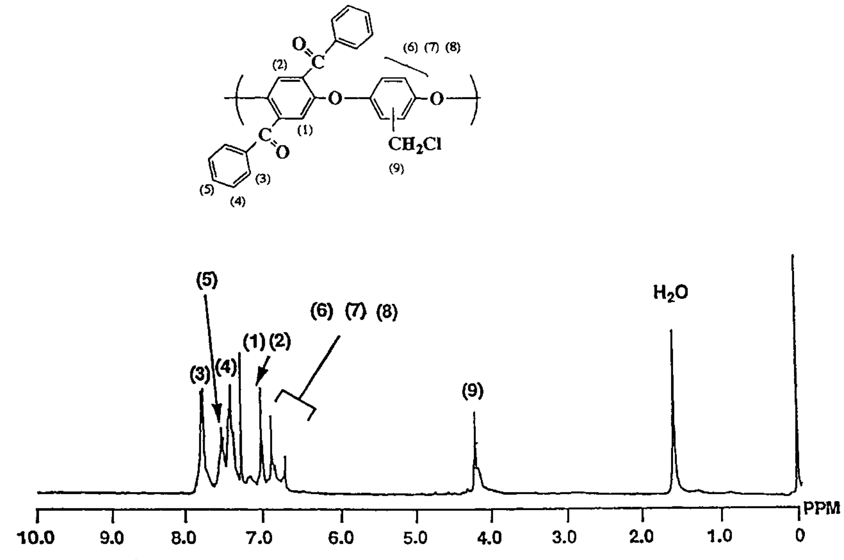


Figure 1 ^1H n.m.r. spectrum of polymer 4

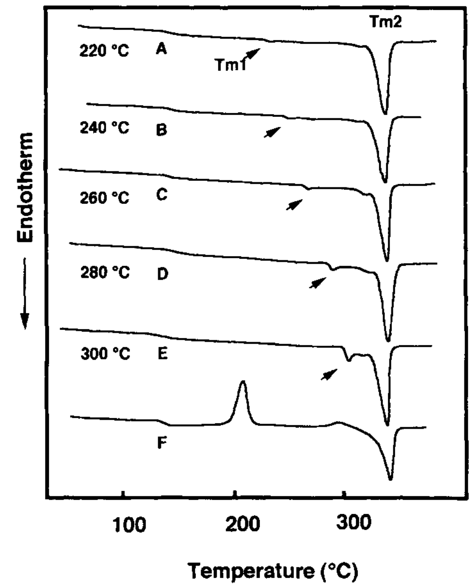


Figure 2 Differential scanning calorimetry heating scans at 20°C min^{-1} for annealed samples at 220°C (a), 240°C (b), 260°C (c), 280°C (d), 300°C (e), for 1 h, and quenched sample (f)

lower- and upper-melting endotherms are plotted *versus* heating rate in *Figures 3 and 4*, respectively. As the heating rate was increased, the lower endotherm peak increased a few degrees, whereas the upper endotherm peak shifted downwards. Furthermore, the heat of fusion of the lower and upper endotherms showed a similar behaviour.

Table 2 Differential scanning calorimetry data and long periods at various annealed temperatures

Annealed temperature (°C)	T_{m1} (°C)	T_{m2} (°C)	ΔH (mJ mg^{-1})	Long period d (Å)[a]
220	235	337	34.2	124
240	252	337	35.6	131
260	270	338	35.2	134
280	287	339	36.0	154
300	306	338	34.9	137

[a] From SAXS data.

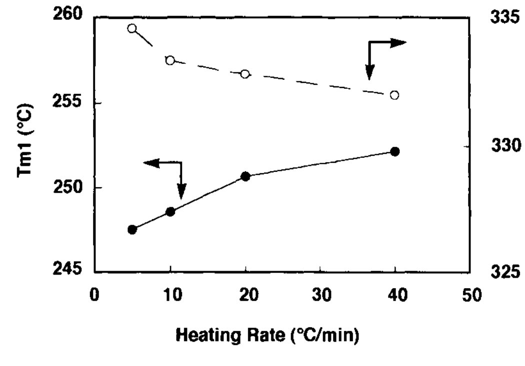


Figure 3 The two melting peak temperature *versus* heating rate, the samples were annealed at 240°C for 1 h

The annealed PEEK samples also showed two melting endotherms in d.s.c. heating scans[11] and the thermal behaviour is comparable to that of the annealed samples tested here. Blundell[11] and Lee and Porter[12] explained this behaviour as follows: the lower endothem is the melting of crystals that exist prior to the heating scan. The upper endotherm is the result of melting of crystals formed by simultaneous melting and recrystallization during the d.s.c. heating scan. The decrease in upper endotherm temperature with increasing heating rate is explained in terms of the shorter reorganization time, that is, the size and perfection of the recrystallized PEEK decreases with increasing heating rate. The raising of the position of the lower peak with heating rate reflects the superheating effect for the onset of the melting position. On the other hand, the reorganization time decreases with increasing heating rate. Therefore, the heat of fusion of the upper endotherm peak bacame smaller. The total heat of fusion for both endotherms decreased slightly with increasing heat rate, due to restricted annealing on heating. These results are consistent with studies on several polymers showing double melting peaks due to the reorganization process.

In *Table 2* it was found that the value of enthalpy (ΔH) and the long period of crystallites depended on annealed temperature. *Figure 5* shows a plot of various annealing temperatures *versus* the density of polymer **3**. As the annealing temperatures was increased from 220 to 280°C, the density increased, which means an increase of crystallinity. This tendency also corresponds to the change in ΔH over long periods. These results indicate that the lamellar thickness also increases with increasing annealing temperature.

Crystallization behaviour of polymer 3

The quenched amorphous sample in *Figure 2* shows precise analogous behaviour to that found with amorphous

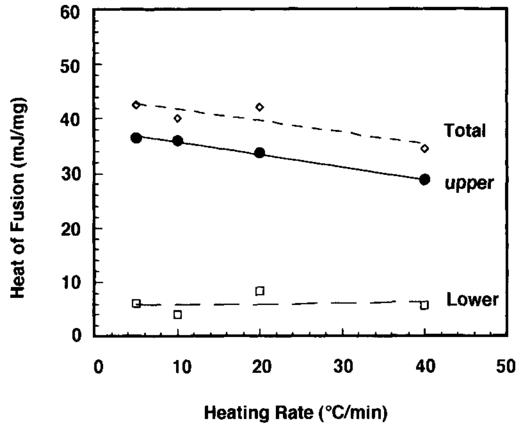


Figure 4 Heats of fusion of the upper- and lower-melting peaks *versus* heating rate, The samples were annealed at 240°C for 1 h

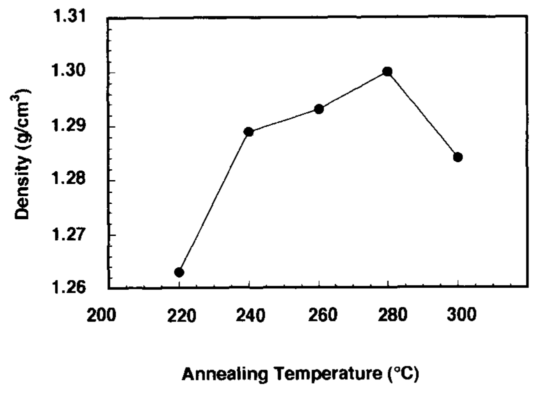


Figure 5 Plot of density *versus* annealing temperature

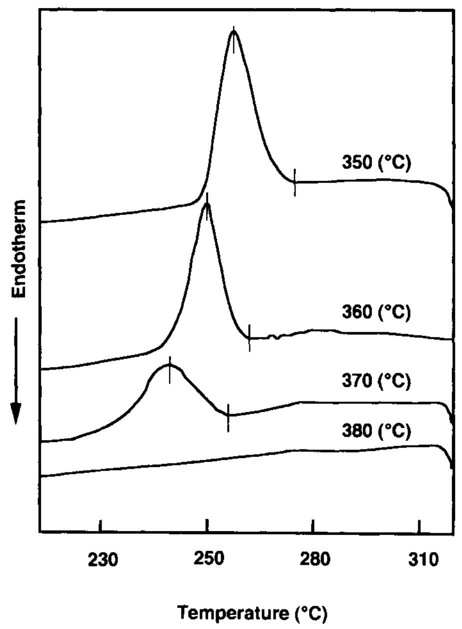


Figure 6 Differential scanning calorimetry cooling curves (−10°C min^{-1}) for powder after melting at various temperatures (350–380°C) for 30 min

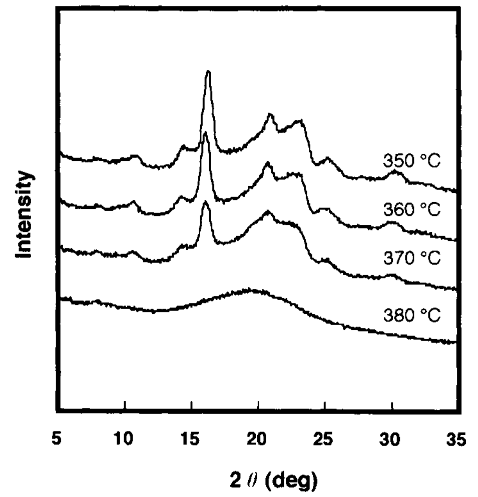


Figure 7 WAXD curves for polymer **3**, the samples were held in the melt for 30 min at various temperatures (350–380°C)

PEEK. There is a T_g step at 134°C, followed by an exothermic peak at 209°C associated with crystallization, and then an endothermic peak at 342°C due to the melting of the crystals.

More informative data on the overall crystallization behaviour are given in *Figure 6*. The sample of polymer **3** was cooled at 10°C min^{-1} after being held in the melt for 30 min at various temperatures (350–380°C). As the melt–annealing temperature was increased, the crystallization exotherm shifted to lower temperatures and became broad, and both onset and peak temperature of the exotherm were decreased. *Figure 7* shows the X-ray diffraction curves for the above samples. The crystallinity decreased as the melt–annealing temperature was increased. Such thermal behaviour was also observed in the PEEK sample and suggested that the number of nuclei decreased with higher melt–annealing temperature, which decreased crystallinity[12].

CONCLUSIONS

Poly[oxy-(2, 5-dibenzoyl-1, 4-phenyleneoxy)-1, 4-phenylene] (**3**) was successfully prepared by the reaction of 2,5-difluoro-4-benzoylbenzophenone with hydroquinone in the presence of potassium carbonate in diphenylsulfone at 320°C.

The d.s.c. analysis showed that polymer **3** annealed at different temperatures (220–300°C) exhibited two distinct endotherms. Annealing treatment shifted the lower peak upwards and the main upper peak remained unchanged. The lower endotherm peak increased a few degrees as the heating rate was increased, whereas the upper endotherm peak shifted downwards. Furthermore, the crystallization exotherm shifted to lower temperatures with an increase in the melt–annealing temperature at above 350°C and crystallinity also decreased. These melting and crystallization behaviours were quite similar to those of PEEK. Therefore, the thermal behaviour of polymer **3** would be explained in terms of the sum of four peaks: melting of most original crystals, their recrystallization, remelting of recrystallized materials, and melting of core crystalline regions, as proposed by Porter *et al.* for the explanation of the double-melting behaviour of PEEK[12].

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